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INORGANIC TRANSPARENT PIGMENTS - OPTICAL PROPERTIES

BY

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Abstract. Requirements for high performance pigments and special pigments led to the development of materials that must comply with the increasingly demanding economic market. Manufacturers of these categories of materials work to produce excellent durability, high colour strength, the excellent dispensability across a wide range of binders, chemical stability and low solubility. The paper presents the current literature information on transparent inorganic pigments and their optical properties. Also, the main classes of transparent inorganic pigments are presented with synthesis, structural properties and applications.

Keywords: transparent inorganic pigments; refractive index; iron oxides; ZnO; TiO_2.

1. Introduction

Inorganic pigments have transparent optical properties when their particle sizes are in the nanometric range, usually below 100 nm. They become

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more transparent as the particles are smaller. Transparent pigments do not reflect light, but allow it to pass through them.

Transparent inorganic pigments may be coloured (iron oxides, cobalt compounds) or colourless (zinc oxide, titanium dioxide). Transparency depends on the light scattered, the size of the pigment particles and the nature of the binder in which it is incorporated. For colourless pigments, light scattering depend on the difference between the refractive indices of the pigment and of the binder. Pigments are materials that change the colour of reflected / transmitted light, due to selective absorption at specific wavelengths. The process is different from luminosity, when an object emits light. Pigments are white, black or coloured, finely dispersed, water-insoluble and solvent-free particles, designed with some chemical and physical properties specific to a particular purpose (Apostolescu and Apostolescu, 2014; Gaedcke, 2009). Visible light is reflected, absorbed, and transmitted in different amounts, depending on the nature of the pigments and of the substrate. Some pigments can reduce the rate at which sunlight is reflected (Dalapati *et al.*, 2018; Gaedcke, 2009).

There are many classes of pigments, such as inorganic or organic, anticorrosive, luminescent, phosphorescent, pearls, thermal, flame retardant, transparent, etc. The classification of inorganic and organic pigments is made using several criteria, as composition, colour, origin or field of use.

Compared to organic pigments, inorganic pigments have a larger average particle size. To obtain a maximum light dispersion, the optimal size of the inorganic particles is between 400 and 800 nm. Organic pigments tend to be much smaller. This is the main cause for which most organic pigments are transparent and most inorganic pigments are opaque. Due to their chemical composition, inorganic pigments are stable in the presence of organic solvents. Usually, inorganic pigments have better temperature stability than organic pigments. However, light resistance and weather resistance vary widely, depending on the nature of the pigment. Inorganic pigments differ from the organic ones by exhibiting higher specific gravity, higher elemental particles, lesser colouring power, higher light and weather resistance, lesser vivid shades, lower oil absorption index (Ceresana, 2018).

The study of inorganic pigments has considerably developed in recent years, due to the need for high-quality, long-lasting decoration materials in the industry. Unlike organic dyes, ceramic dyes have a high chemical and temperature resistance, definition of shades, and a long life, with superior properties.

The selection of a pigment that meets the conditions imposed by its use requires a number of factors to be taken into account such as: colour, uniformity and reproducibility of the pigment, average particle size, compatibility of the pigment with the components of the system in which they are introduced and, last but not least, its thermal stability.

In Europe, a number of 573 pigments were developed that are commercially available. Of these, nearly 200 were registered under REACH by September 2014. The list does not contain fine metal particles such as: aluminium and copper used for pigment applications (Hynes *et al*., 2018; Sørensen *et al*., 2015).

Globally, the most used pigments are titanium dioxide, carbon black and iron oxides. In the EU, titanium dioxide represents about 70% of the total volume of applied pigments, other inorganic pigments about 25% and about 5% organic pigments. The total volume of the European pigment market is estimated at around 2,220,000 tons in 2013 and appears to grow slightly (Sørensen *et al*., 2015).

2. Optical Properties

Light (electromagnetic radiation) when reaches any object has three possibilities: it can be reflected, absorbed or transmitted (Fig. 1). Independently or together, these three types of effects may appear totally or selectively across the spectrum of electromagnetic radiation (it results that a substance may reflect in the visible region, absorb in the UV region and transmit in the infrared region or any other combination of the three).

Transparency is the physical property of a material that allow light to pass through, without being scattered. Any object that has smaller measures than 380 nm (the visible light wavelength) is transparent. Particles about, for example, 100 nm are not visible. However, this happens only in extraordinary circumstances: as soon as more particles are found together, the light passes through the white colour and becomes visible again due to the diffraction or dispersion. However, not all the chemical and physical properties of the particles change when they become nanoparticles. Absorption properties, for example, persist, *i.e*., the particles no longer reflect light, so they are transparent, but absorb UV radiation.

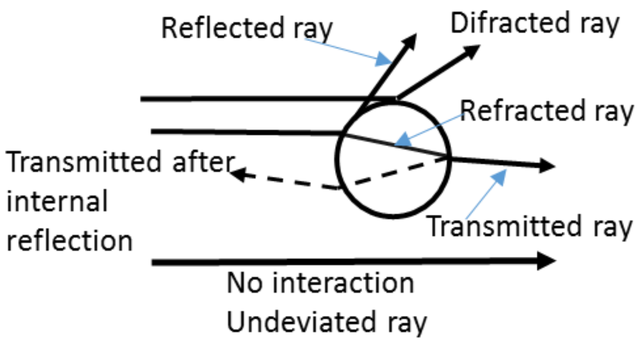

Fig. 1 − The processes occurring in the propagation of light (Rawlings *et al*., 2013).

Absorption of electromagnetic radiation depends on the wavelength of the radiation, the nature and structure of the material. In case of a material of thickness l, the intensity of the radiation coming out of material (neglecting the reflected radiation) can be expressed by the relation:

$$I_l = I_0 \cdot e^{-K \cdot l} \tag{1}$$

where I_0 is the of incident radiation and K is the absorption coefficient; Transparency or transmission is due to the difference between the intensity, *i.e.*:

$$T = I_0 - I_l \tag{2}$$

The pigment particle becomes transparent in binders when the difference between the refractive index of the pigment (depending on its wavelength and its colour) and of the binder, $\Delta n = n_p - n_l$, is as small as $\Delta n \rightarrow 0$, or the dimensions of the pigment particles are in the range 2-150 nm.

The crucial factor for transparency is usually the particle size and the direction that light passes.

The colour of the substances is determined by the spectral absorption and reflection characteristics, the shape, position and intensity of the spectral curves, depending on the chemical structure, polymorphism, the shape, size and distribution of the dyestuff particles (Buxbaum and Pfaff, 2005).

Applying a transparent or semi-transparent film to a matte surface comes with spectacular optical effects, the colours become deeper and brighter and the contrast between colours is more obvious. Interference of light waves is a source of colour, and occurs when a thin film of transparent substrate is applied on a reflective surface. Solid pigment particles in a coating are able to change the direction of light rays when the particles and the matrix surrounding them have different refractive index *n*. The efficiency of the phenomenon called *scattering* results in the covering power of the coating and is governed by few properties (Fig. 2).

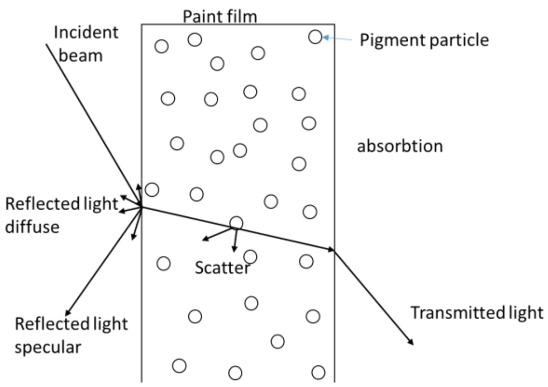

Fig. 2 − Light Interactions in a Semi-Transparent Film.

It is very important to realize that scattering is not a consequence of the surface but involves the entire particle.

First, scattering is strong when the difference in refractive index values for the particle and matrix, $\Delta n = n_p - n_m$, is big. The refractive index of a material is conditioned by its chemical composition. Secondly, for a specific wavelength, λ, there is an optimum regarding the particle size. The optimal particle diameter d for scattering light is about half of the wavelength of the light (Beetsma, 2017b), as is shown in Fig. 3.

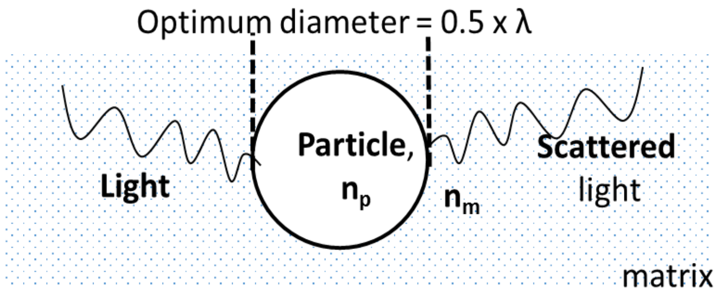

Fig. 3 – Particle optimum diameter for scattering (Beetsma, 2017b).

Experimental, the transparency of a pigment is determined by measuring the colour difference between a sample of a pigmented system on a black background and the uncovered background.

3. Transparent Pigments Synthesis and Properties

For a pigment of a certain chemical composition, transparency is influenced by the synthetic conditions and the size of the primary particles, respectively. For pigments with small primary particles, there is always a tendency for agglomeration, a phenomenon that can be cured with great difficulty, either by mechanical action or by the addition of additives during synthesis. The most used additives are the sodium salts of fatty acids or higher alkyl amines which greatly diminish the agglomeration tendency.

Transparent pigments, with nanometer-sized particles, have a specific surface area (BET) of more than 100 m^2/g, which results in an increase of the oil index.

Many transparent inorganic pigments are described in the literature, the most widely used are shown in Table 1 with their main applications. Some transparent pigments are produced only for special applications, and are not suitable for industrial scale (Pfaff, 2017).

Table 1
The Most Important Transparent Pigments

Pigment type	Particle size	Applications	References
Iron Oxides	10-200 nm	automotive paints, wood coatings, plastics applications, industry coatings, printing ink, art, cosmetics	Sørensen *et al*., 2015; Parkinson, 2016; Lu, 2017
Zinc oxide	150 nm 10-20 nm	wood and paper coatings, UV-blocking, transparent bactericidal oxide coatings	Afsharpoura and Imani 2017; Evstropiev *et al*., 2017; Moezzi *et al*., 2012
Titanium dioxide	< 300 nm	sunscreen antimicrobial applications, air and water purification, medical applications, energy storage	Weir *et al*., 2012; Ceresana, 2018; Pfaff, 2017
Cobalt aluminate $CoAl_2O_4$	20-100 nm length and about 5 nm thick	metallic paints, very good resistance to weathering and light	Wang *et al*., 2016; Zhang *et al*., 2018

Transparent Iron Oxides

The most iron oxide pigments are coloured, involving the absorption and scattering of a part of the visible light. For some applications pigments absorb some visible radiation, and for others they scatter. Iron oxides can be found in a large colour range, including yellow (goethite), orange (lepidocrocite), red (hematite), black (magnetite) and grey (wustite).

If the particles are around 10-20 nm diameter, the iron oxide pigments are transparent, as shown in figure 4 (Beetsma, 2017a; Mohapatra and Anand, 2010).

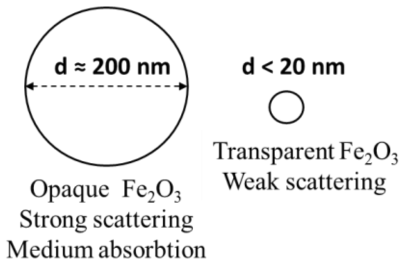

Fig. 4 – Optical properties of opaque and transparent nano-sized Fe_2O_3 particles (Beetsma, 2017a).

The different colours of iron oxides are given by the displacement of the absorption band due to the charge transfer (electron transfer reaction) between the ligand (OH^- or O^{2-}) and the Fe^{3+} ion, followed by the loss of Fe^{3+} ion symmetry, for example the transition p orbital (from O^{2-} or OH^-) to the metallic centre of the Fe^{3+} ion (3d orbital) (Müller *et al.*, 2015). Their colours are a result of differences in the structural arrangement as well as the size of the particles. The most used iron oxide transparent pigments are shown in Table 2.

Table 2
Iron Oxide Transparent Pigments

Pigment type	Chemical composition	Oxidation level of the iron	Crystal system, obs.
Iron oxide red (hematite)	α-Fe_2O_3	Fe(III) ions	trigonal
Iron oxide yellow (goethite)	α-FeOOH	Fe(III) ions	orthorhombic
Iron oxide orange (lepidocrocite)	γ-FeOOH	Fe(III) ions	orthorhombic
Iron oxide black (magnetite)	Fe_3O_4	Fe(II) and Fe(III) ions	isometric, spinel structural group
Iron oxide grey (wustite)	($Fe_{1-x}O$)	Fe(II) ions	isometric, crystal habit: pyramidal, prismatic

The **transparent yellow oxide**, α-FeO(OH), has the structure of the goethite; by heating it a transparent red oxide film α-Fe_2O_3 with a hematite structure form around the particle. After a short heat treatment, the orange shade appears which can also be obtained by direct mixing of the yellow and red iron oxide powders.

The transparent yellow iron oxide pigment is obtained by precipitating ferrous hydroxide or ferrous carbonate solution with an alkali hydroxide or carbonate, followed by oxidation to FeO(OH). Industrially, oxidation is achieved by bubbling air into the reaction mixture. The optimal parameters that lead to good transparency are: diluted ferrous sulphate solutions (5-6%), 10% carbonate solution, temperature below 25°C, and air bubbles. Preparation of transparent iron yellow can be done by several methods such as: ferrous conversion method (acid method and the alkali method), ferric iron conversion and direct conversion method (Lu, 2017; Müller *et al.*, 2015).

The transparent red oxide pigment can be obtained directly by precipitation from the ferrous solution in the form of hydroxide or carbonate at about 30°C, and the oxidation is carried out completely in the presence of additives such as magnesium, calcium or aluminium.

Transparent red oxide can also be obtained by spraying in an atomizer the iron pentacarbonyl solution, in excess air, at a temperature of 580-800°C. The resulting product has primary particles of about 10 nm, amorphous, irregular shapes and red-orange shades.

Brown iron oxide pigment is obtained by precipitating ferrous solutions with dilute alkali solutions (sodium hydroxide or carbonate) and oxidation by air.

Transparent pigments based on ferric oxides have similar properties to conventional pigments in terms of light, weathering and chemicals resistance. In addition, they strongly absorb the ultraviolet radiation, a property used in their application in colouring plastic bottles and thin films of ultraviolet-sensitive food wrapping paper. They are also used in the manufacture of metallic paints, in combination with aluminium pigments, in architectural coatings, in the colouring of bottles and ampoules, automotive and wood coatings, art paint and tobacco packaging and many more (Baghaie *et al*, 2011; Zlamal *et al*., 2017; Parkinson 2016, Pfaff 2017). Some manufacturers report the production of transparent pigments from recycled waste or secondary products (Hajjaji *et al*., 2012; Ovčačíková *et al*., 2017).

Transparent cobalt pigments

The transparent blue cobalt pigment ($CoAl_2O_4$) - cobalt aluminate blue is obtained by precipitating cobalt and then aluminium over the previously formed particles, as hydroxides or carbonates, from their solutions, according to the reaction presented in Eq. (3) (Buxbaum, 2005; Pfaff, 2017).

$$2\mathrm{Al(OH)_3} + \mathrm{Co(OH)_2} \rightarrow \mathrm{CoAl_2O_4} + 4\mathrm{H_2O} \quad (3)$$

Precipitation is done with alkaline solutions. It is very important to use diluted solutions, so the distribution of alkali to be uniform throughout the volume. The precipitate, after filtration, was washed, dried and calcined at 1000°C. The pigment particles are very fine, the primary particles having hexagonal shapes, 20-100 nm length and about 5 nm thick, and the BET specific surface area of about 100 m^2/g; although it exhibits very good resistance to weathering and light, very good chemical stability, has limited uses, especially for the preparation of metallic paints and it's still a niche product. $CoAl_2O_4$ ultrafine can also be prepared by the modified Pechini method, starting from nitrates ($Co(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$) as an oxidant, glycine as fuel and carbon as a sacrificial agent, obtaining aggregates of 5-10 nm with excellent optical properties (Jafari and Hassanzadeh, 2014, Wang *et al*., 2016). Recently, a $CoAl_2O_4$ / kaolin hybrid pigment has been used to make a heat-resistant, self-cleaning paint (Zhang *et al*., 2018; Assis *et al*., 2016) and the scientific community is working to improve and diversify the properties.

Transparent zinc oxide

Similar to titanium dioxide, the zinc oxide pigment can be white or transparent. Transparent zinc oxide pigment also has, multiple applications such as: antimicrobial, UV-blocking agent, UV sensor devices; food packaging application, ceramic industry, cosmetics, etc. (Besleaga *et al*., 2012; Han *et al*., 2015; Izumi *et al*., 2009; Dhapte *et al*., 2015). The ZnO nanoparticles are manufactured using precipitation processes in the presence of protective colloids to limit particle growth. An industrial process uses solutions of zinc sulphate and zinc chloride in a 1:2 ratio. The basic carbonate is precipitated by simultaneous mixing of the zinc solution with sodium hydroxide or carbonate, the precipitate being thoroughly washed and then dried. An industrial process to obtain transparent ZnO consists of combustion of high purity Zn in pressurized chambers in the presence of oxygen, according to the reaction described by Eq. (4), when the primary particles are less than 30 nm:

$$2\mathrm{Zn} + \mathrm{O_2} \rightarrow 2\mathrm{ZnO} \tag{4}$$

Another process consists in the hydrolysis of zinc organic compounds, according to the Eq. (5), the primary particles being below 15 nm, but the process is more expensive (Pfaff, 2017):

$$\mathrm{Zn(OR)_2} + \mathrm{H_2O} \rightarrow \mathrm{ZnO} + 2\mathrm{ROH} \tag{5}$$

Transparent titanium dioxide

In 2017, more than 15 million tons of TiO_2-containing minerals have been processed worldwide and about 60% of these were processed to obtain TiO_2-pigments (Ceresana, 2018).

Titanium dioxide (rutile or anatase) with primary particles smaller than 100 nm has transparent properties (Fig. 5).

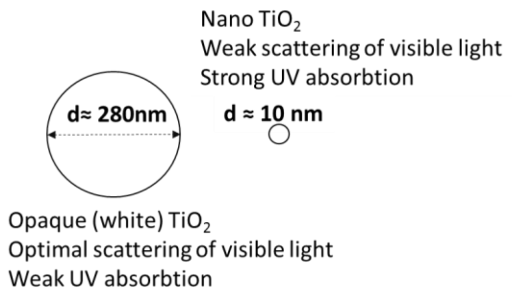

Fig. 5 – Optical properties of opaque and transparent nano-sized TiO_2 particles (Beetsma, 2017a).

Its uses as a white pigment are limited, as diffused light scattered by very small particles is very low, which makes the colouring effect insignificant. The physical properties of nanometric titanium dioxide are significantly changed from those of the conventional pigment. It has a strong ultraviolet absorption as well as a high photoconductivity. Based on these properties, it is used as an additive in many products, either as a heat stabilizer or as a non-toxic absorber of ultraviolet radiation. TiO_2 is a versatile material with ever-growing applications, from the worldwide production around 30% is used as a pigment, 10% in plastics, 6% in paper industry and the rest in specific fields, as cosmetics, especially for glowing and UV absorbing effect, ensuring skin protection; for automotive paints, in particular powder - aluminium foil, which prints out the side effect, the intensity of the effect being related to the concentration in nanometric titanium oxide; for clearing varnishes used for wood preservation; for plastics protection against photodegradation; as a heat stabilizer for silicone rubber or as a catalyst for the hydrogenation and oxidation process (Abdullah and Kamarudin, 2017; Cavalcante *et al*., 2009; Dalapati *et al*, 2018, Gholami *et al*., 2017; Meenakshi and Selvaraj, 2018). The titanium dioxide used in food and personal care products hasparticle size between 40-220 nm diameters (Weir *et al*., 2012).

For transparent TiO_2 synthesis, many processes can be applied, some of them only starting from rutile. The basic reactions of these processes are described by Eqs. (6-10) (Buxbaum and Pfaff, 2005; Pfaff, 2017):

$$\mathrm{TiOSO_4 + H_2O \rightarrow TiO_2 + H_2SO_4}\ \text{(anatase)} \tag{6}$$

$$\mathrm{TiOCl_2 + H_2O \rightarrow TiO_2 + 2HCl}\ \text{(rutile)} \tag{7}$$

$$\mathrm{TiCl_4 + 4NaOH = TiO_2 + 4NaCl + 2H_2O} \tag{8}$$

$$\mathrm{Na_2TiO_3 + 2HCl = TiO_2 + 2NaCl + H_2O} \tag{9}$$

$$\mathrm{Ti(OC_3H_7)_4 + 2H_2O = TiO_2 + 4C_3H_7OH} \tag{10}$$

The stages of manufacturing processes includes: precipitation, filtration and washing, followed by drying and dimension reducing (a very important step). Nanoparticles are often “wrapped” with various inorganic compounds (*e.g*. silica, alumina, zirconium or iron oxides), similarly to the conventional titanium dioxide pigment.

Nano-titanium dioxide can be produced by a gaseous process, at 700°C, based on the following reaction described by Eq. (11):

$$\mathrm{TiCl_4 + 2H_2 + O_2 \xrightarrow{700\ C} TiO_2 + 4HCl} \tag{11}$$

Annual consumption of transparent titanium dioxide is increasing and is estimated at around 1300 t/year, being marketed under different names:

Transparent titanium dioxide (Ishihara, Japan and Kemira Oy, Finland), titanium dioxide P25 (Degussa, Germany) and MT titanium dioxide (manufacturer Tayca, Japan).

Transparent titanium dioxide pigments can be used to produce frost effects and shadow changes in coatings combined with other coloured pigments.

The frost effect is obtained by the alternative application of transparent pigments and metallic pigments.

A certain colour change effect can be observed by the human eye when changing the viewing angle of the coated surface.

The explanation of this effect is based on a different interaction of the visible spectrum light with TiO_2 nanoparticles. The red and green parts of the spectrum are only slightly scattered, while the blue parts are scattered strongly by the TiO_2 particles and leave the coated surface at a small angle.

In this way, the change of shades in pigmented coatings with coloured pigments by adding a transparent TiO_2 pigment does not depend on the viewing angle.

Issues related to the risks of using transparent pigments

For regular users, theoretically the most relevant exposure route from paint containing transparent pigments is dermal contact and therefore the risks are considered to be low. Although oxide pigments have limited reactivity at nanometric levels, their physicochemical properties and toxicity differ as compared to bulk material. But in the absence of precise data on toxicity and exposure to transparent nano-pigments, it is necessary to consider all the ways in which they can affect living organisms and all possible interactions. Some studies shows that in nanoscale form, ZnO or TiO_2 (ingested) are more aggressive than bulk (Boon *et al*., 2010; Srivastav *et al*., 2016, Shakeel *et al*., 2016).

4. Conclusions

Transparent inorganic pigments are a category of materials that has developed rapidly over the past few years due to their special properties such as: optical effects, chemical resistance, low cost, low toxicity, or high-capacity absorption of ultraviolet radiation. Transparent inorganic pigments belong to the nanomaterials category because they are small in size (primary pigment nanoparticles and their agglomerations do not scatter light). Transparent inorganic pigments may be colourless (TiO_2, ZnO) or coloured (pigments of iron, cobalt, etc.) and can be used in many industrial fields. In terms of toxicity and induced risks, transparent pigments are associated with nanomaterials, are subject to regulations in force and are still being investigated.

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PIGMENȚI ANORGANICI TRANSPARENȚI – PROPRIETĂȚI OPTICE

(Rezumat)

Cerințele pentru pigmenții de înaltă performanță și pigmenții speciali au dus la dezvoltarea unor materiale care trebuie să respecte condițiile din ce în ce mai exigente ale pieței economice. Producătorii acestor categorii de materiale lucrează pentru a produce durabilitate excelentă, rezistență ridicată a culorii și dispersabilitate excelentă, într-o gamă largă de lianți, stabilitate chimică și solubilitate scăzută. În lucrare se prezintă stadiul actual al literaturii de specialitate privind pigmenții anorganici transparenți precum și proprietățile lor optice. De asemenea sunt prezentate principalele clase de pigmenți anorganici transparenți cu metode de obținere, proprietăți structurale și aplicații.